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Energy Transfer in Micellar Systems. Steady State and Time Resolved Luminescence of Aqueous Micelle Solubilized Naphthalene and Terbium Chloride

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Abstract: Efficient energy transfer has been demonstrated from micellar sodium dodecyl sulfate (SDS) solubilized naphthalene to terbium chloride. In the absence of micelles there is no energy transfer. The role of micelles is to allow the compartmentalization of no more than one donor into each micellar interior and at the same time to concentrate large number of acceptor molecules at the micellar surface. ^{1}H NMR spectroscopic techniques have established the substantial binding of terbium chloride to the surface of SDS micelles. The photophysical mechanism involves energy deposition in naphthalene, excitation into singlets, intersystem crossing into the triplet domain, and diffusion of naphthalene triplets to the micellar surface where energy transfer to terbium chloride occurs. In water, triplet-triplet annihilation prevents energy transfer. The lifetime of naphthalene triplet in micellar SDS has been determined to be at least $(1.14 \pm 0.07) \times 10^{-5}$ s; the time for its diffusion not of the micellar interior has been estimated to be 2.62×10^{-7} s. The significance of these results is discussed.

Organization of reactants into suitable compartments is an inherent property of biological systems.[1] Boundaries of the compartments are defined by the cell membrane. Many complex enzymatic and electron transport systems are membrane bound. Proximity, favorable orientation, and microscopic environment are factors which contribute to the required optimization of the appropriate process. Considerable understanding of membrane-mediated interactions has been obtained through the investigations of model systems. Aqueous and reversed micelles,[2,3] black lipid membranes,[4] and liposomes[5-7] have been used as models. Determinations of energy transfer from a photoexcited donor to an acceptor, localized in different parts of given membrane models, can provide significant structural information.[8] Energy transfer efficiencies are likely to be different in membrane models than those in bulk water. Indeed energy transfer from diphenyloctatetraene to chlorophyll is 4-5 times more efficient in the environment of black lipid membranes or of liposomes than that in water.[9] These increased efficiencies coupled with suitable partitioning may well pave the way to the design of economically feasible solar energy conversion.[10,11] Additionally favorable organization of the different ground and excited state species are likely to alter, if not simplify, the photophysics involved. Fundamental information on mechanistic photophysics can be gained therefore by investigating appropriate systems in model environments.

We have initiated studies into energy transfer in systems which mimic facets of biomembranes. Our attention is primarily focused on well-characterized models which can organize donor and acceptor molecules in a recognizable manner. Details of energy transfer from naphthalene to terbium chloride in the presence of aqueous micellar sodium dodecyl sulfate are reported in the present paper. Energy transfer in the naphthalene-terbium chloride system is theoretically possible, but owing to low efficiency, it cannot be observed in homogeneous fluids at room temperature.[12] Naphthalene, in fact, quenches the energy transfer to terbium chloride from several ketones.[12] Conversely, we have observed energy transfer from micelle solubilized naphthalene to terbium chloride. Aqueous micellar sodium dodecyl sulfate was chosen as membrane model since effective partitioning of naphthalene to the micellar interior has been demonstrated and since the relatively small but highly charged terbium cation is likely to be attracted to the negatively charged Stern layer. Since the aggregation number of this micelle is well known,[2,13] the number of donor and acceptor molecules per micelle can be readily assessed. The ability of the micelle to organize these energy transfer partners renders, we feel, this study to be an appropriate model for biological energy transfer.

Experimental Section

Sodium dodecyl sulfate (SDS), gel electrophoresis grade (99.7%), was obtained from BioRad Laboratory. Its reported purity was verified by comparing the absorption spectrum and surface tension behavior with those of an authentically pure (>99.9%) sample kindly donated to us by Kao Soap Co., Japan. Hexadecyltrimethylammonium bromide (CTABr, Sigma) was used as received. Terbium chloride hexahydrate (99.9% pure, Alfa-Ventron) was used without further purification. Good agreement between the observed and reported absorption and emission spectra[12] verified the purity of this compound.

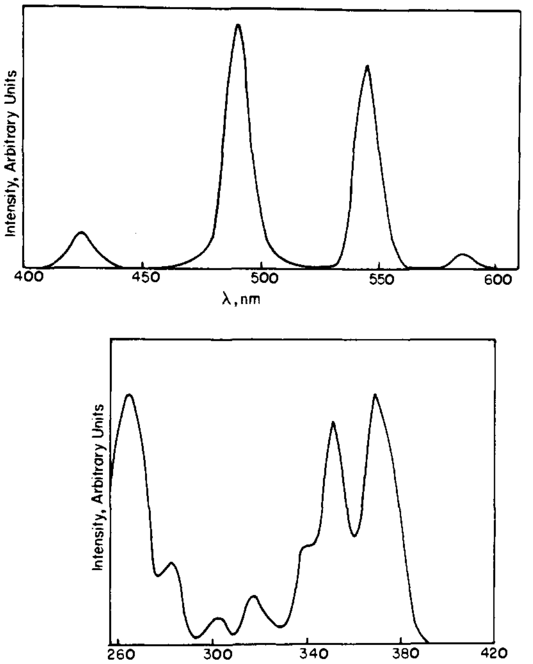

Figure 1. Emission (excited at 370 nm) spectrum (top) and excitation (using emission wavelength of 491 nm) spectrum (bottom) of 0.010 M $TbCl_3$ in 0.20 M SDS containing 0.01 M sodium acetate-acetic acid buffer at pH 5.0.

Naphthalene (scintillation quality, MCB) was purified by sublimation. Deionized water was distilled in an all-glass still. All the other chemicals were the best available reagent grade and were used without further purification.

All experiments were carried out in 0.20 M SDS in the presence of 1.0×10^{-2} M sodium acetate-acetic acid buffer at pH 5.0 unless otherwise specified.

Absorption spectra were taken on a Cary 118C recording spectrophotometer. Steady state corrected luminescence spectra were obtained on a SPEX Fluorolog spectrofluorometer using its E/R mode and 2.5-mm slits using a band path of 10 nm. Fluorescence lifetimes were determined by means of a modified Ortec 9200 single photon counting nanosecond time resolved fluorescence spectrometer,[14,15] with the output displayed on a multichannel analyzer. Excitation wavelength was selected by the use of a 280-nm filter (Ditric Optics, Inc.) with a 15-nm HHBW. Fluorescence lifetimes were calculated either graphically[16] or on an IBM 360 computer using the method of moments program.[17] Since fluorescence lifetimes observed in the present work far exceeded the half-width of the lamp pulse (ca. 2 ns) computer-calculated lifetimes agreed well with those determined graphically. Phosphorescence lifetimes were determined by the phosphorescence attachment of the SPEX Fluorolog.[18] All spectral work was carried out at 25.0 ± 0.1 °C. Luminescence spectra and lifetimes for all solutions were determined on degassed samples. Degassing was carried out on a high-vacuum line using repeated freeze-pump-thaw cycles.

^1H nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer at ambient probe temperature (33 °C). Solutions were freshly prepared in D_2O. Chemical shifts were measured relative to external Me_4Si, contained in a Wilmad 520-2 capillary tube. Chemical shifts were obtained from spectra recorded at 500-Hz sweep widths and they are accurate within ±0.2%.

Results

Interaction of Terbium Chloride with Aqueous Micelles. Terbium chloride, $TbCl_3$, is highly soluble in water. Its absorption in the ultraviolet and visible region is extremely weak. Molar absorptivities of 1.0 M aqueous $TbCl_3$ at the absorption maxima were found to be $\epsilon_{284nm} = 0.37$, $\epsilon_{295nm} = 0.11$, $\epsilon_{303nm} = 0.15$, $\epsilon_{318nm} = 0.17$, $\epsilon_{327nm} = 0.09$, $\epsilon_{336nm} = 0.10$, $\epsilon_{339nm} = 0.16$, $\epsilon_{342nm} = 0.17$, $\epsilon_{351nm} = 0.30$, $\epsilon_{358nm} = 0.17$, $\epsilon_{369nm} = 0.31$, $\epsilon_{377nm} = 0.20\ M^{-1}\ cm^{-1}$. Excitation of 1.0×10^{-2} M aqueous $TbCl_3$ at 370 nm resulted in weak emissions, centered at 415, 491, 541, and 586 nm. This luminescence spectrum agreed well with that reported previously.[12] Utilizing the terbium emission at 491 nm, the determined excitation spectrum, although less well resolved, was essentially identical with the absorption spectrum.

Table I. Effect of SDS on $TbCl_3$ Luminescence[a]

[SDS],[b] M	RI_{491nm}[c]	RI_{546nm}[c]
0	1.00	1.00
0.05	0.98	0.98
0.10	1.05	1.04
0.20	0.98	0.97
0.30	1.01	0.94
0.40	0.94	0.95
0.50	1.05	0.99

[a] In 0.01 M acetate buffer at pH 5.0. [b] $[TbCl_3] = 0.005$ M. [c] Relative luminescence intensities. Excitation wavelength of 370 nm.

Addition of equimolar amounts of sodium dodecyl sulfate (SDS), precipitated $TbCl_3$. The formed compound, presumably terbium dodecyl sulfate, $Tb(DS)_3$, readily redissolved, however, in excess SDS. $Tb(DS)_3$ complex was solubilized by the SDS micelles. All investigations were carried out in homogeneous solutions of $TbCl_3$ in the $(5.0\text{–}20) \times 10^{-3}$ M range and generally in the presence of 0.20 M micellar SDS. Excitation and emission spectra of SDS solubilized $TbCl_3$ were in all cases identical with those observed in pure water. Figure 1 illustrates typical excitation and emission spectra of $TbCl_3$ in aqueous micellar SDS. Lack of changes of $TbCl_3$ luminescence as a function of SDS concentration (Table I) suggests that the Tb(III) cation retains water in its coordination sites[19] and that it is predominantly solubilized in the highly charged Stern layer of the micelle.

More intimate information on the interaction of $TbCl_3$ with micellar SDS is obtained by examining the ^1H NMR parameters of the magnetically discrete surfactant protons in the absence and in the presence of $TbCl_3$. The observed chemical shifts in 0.20 M SDS at 1.36, 1.76, and 4.50 ppm (downfield from Me_4Si) due to the terminal methyl, the intermediate methylene, and the methylene protons next to the sulfate head group, respectively, agreed well with those previously reported.[20] Addition of increasing amounts of $TbCl_3$ to 0.20 M SDS resulted in upfield shift of magnetically nonequivalent surfactant protons. As expected, the C-1 methylene protons (i.e., next to the sulfate head group) experienced the most pronounced alteration as a function of added $TbCl_3$ (Figure 2). These data fully support the proposed interaction of $TbCl_3$ at the hydrated micellar surface. Alteration of chemical shifts with added $TbCl_3$ is paralleled with line broadening. At $TbCl_3$ concentration 0.02 M, in fact, a complete collapse of the spectrum occurs. Line broadening of the $(CH_2)_{10}$ protons showed a typical saturation behavior (Figure 3). These data were used for the estimation of the binding constant, K, for the association of SDS micelles, M, with $TbCl_3$ to give the terbium-micelle complex, TbM:

$$M + TbCl_3 \overset{K}{\rightleftharpoons} TbM \qquad (1)$$

from the relationship[21]

$$\log \frac{\nu_{Hz}{}^{2} - \nu_{Hz}}{\nu_{Hz} - \nu_{Hz}{}^{o}} = -\log K + \log\,[TbCl_3] \qquad (2)$$

where $\nu_{Hz}{}^{s}$, ν_{Hz}, and $\nu_{Hz}{}^{o}$ are half-height bandwidths at saturation, intermediate $TbCl_3$ concentrations, and in the absence of the paramagnetic ion. Treatment of the available data according to eq 2 resulted in an estimated value of $K = 500 \pm 100\ M^{-1}$. There is, therefore, an appreciable binding between

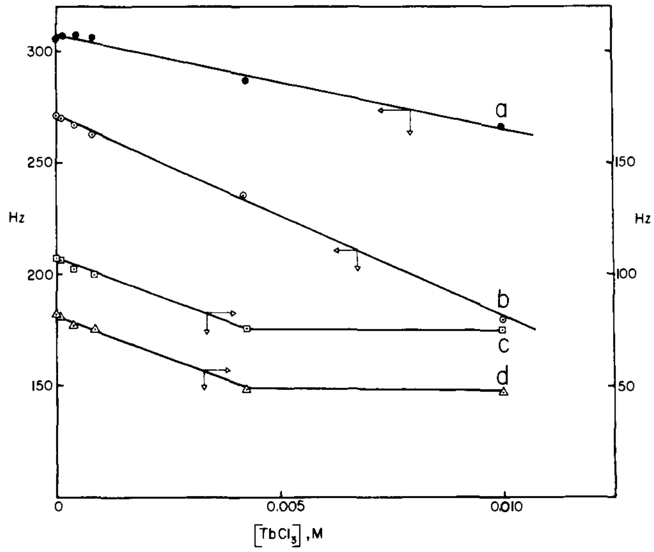

Figure 2. Plot of chemical shifts for HOD (a), $CH_3(CH_2)_{10}C\mathit{H}_2OSO_3^-Na$ (b), $CH_3(C\mathit{H}_2)_{10}CH_2OSO_3^-Na^+$ (c), $C\mathit{H}_3(CH_2)_{11}OSO_3^-Na^+$ in 0.20 M SDS in D_2O as a function of $TbCl_3$ concentration.

Table II. Relative Intensity of $TbCl_3$ Luminescence as a Function of Naphthalene and $TbCl_3$ Concentrations[a]

10^4[naphthalene], M	[$TbCl_3$], M	RI[b]
	0.010	1.0
0.10	0.010	13.0
0.30	0.010	30.0
1.00	0.005	37.1
1.00	0.010	68.3
1.00	0.015	85.7
1.00	0.020	92.9
2.00	0.010	77.1
3.00	0.010	58.6
10.00	0.010	45.7

[a] [SDS] = 0.20 M in 0.01 M acetate buffer at pH 5.0. [b] Excitation wavelength 282 nm; emission wavelength 491 nm.

micellar SDS and $TbCl_3$. Significantly, line widths of the proton magnetic resonances of cationic micellar hexadecyltrimethylammonium bromide are unaffected by added $TbCl_3$ (Figure 3). This is the expected result, of course, since cationic micelles repel the positively charged Tb(III).

Interaction of Naphthalene with Aqueous SDS. Naphthalene is not very soluble in water. It is readily taken up, however, into the hydrocarbon-like interior of aqueous micellar SDS. Lack of quenching by sodium bromide of SDS solubilized naphthalene fluorescence is in accord with this mode of substrate-micelle interaction.[22] Molar absorptivities of SDS solubilized naphthalene, $\epsilon_{259nm} = 3.4 \times 10^3$ (sh), $\epsilon_{267nm} = 5.0 \times 10^3$, $\epsilon_{278nm} = 5.5 \times 10^3$, and $\epsilon_{285nm} = 3.6 \times 10^3$ M^{-1} cm^{-1}, were found to be in agreement with those observed in pure water.[23] Excitation of 10^{-4} M naphthalene in 0.20 M SDS at 282 nm resulted in an emission band centered at 335 nm. The excitation spectra of naphthalene in 0.20 M SDS and in water (using 335 nm emission) agreed well with the observed absorption spectra. The fluorescence lifetime of naphthalene in 0.20 M SDS, 76 ns, is somewhat longer than that reported previously under slightly different experimental conditions (60 ns in 0.03 M SDS).[22] This discrepancy is likely due to the lower concentrations of dissolved oxygen in the present system. Since SDS does not absorb the light appreciably above 230 nm, it does not interfere with the energy transfer.

Energy Transfer. Addition of (1.0-2.0) $\times 10^{-4}$ M naphthalene to 0.10 M $TbCl_3$ in the presence of 0.20 M micellar SDS resulted in a remarkable enhancement of the intensities of the Tb(III) emission bands (Figure 4). Excitation spectra of the same solutions (taken in the 250-400-nm region using 491 or 546 nm as emission wavelength) showed the appearance of several new bands in the 250-300-nm region in addition to those due to Tb(III), which remained unaltered in position and intensity in the presence of added naphthalene. The new excitation bands were identical with those of naphthalene in SDS and are in excellent agreement with the reported excitation spectrum of naphthalene.[24] Since naphthalene does not emit at the wavelength at which the excitation spectrum was analyzed (491 and 546 nm) these results are clear manifestations of energy transfer from naphthalene to Tb(III) via an excited state.

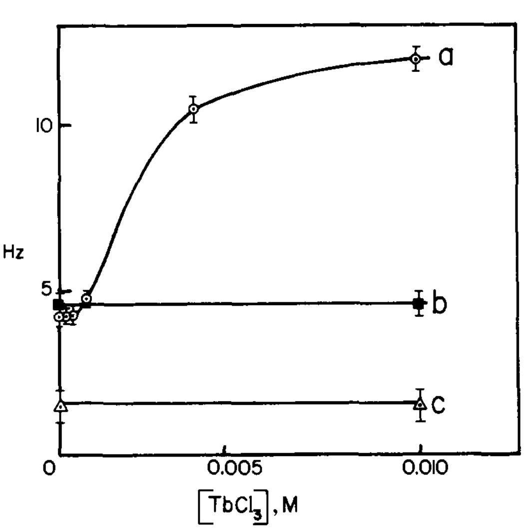

Figure 3. Plot of ^1H NMR line width at half-height for $CH_3(C\mathit{H}_2)_{10}CH_2OSO_3^-Na^+$ protons in 0.20 M SDS in D_2O (a), for $CH_3(C\mathit{H}_2)_{14}CH_2N^+(CH_3)_3Br^-$ in 0.20 M CTABr in D_2O (b), and for $CH_3(CH_2)_{14}CH_2N^+(C\mathit{H}_3)_3Br$ in D_2O as a function of $TbCl_3$ concentration.

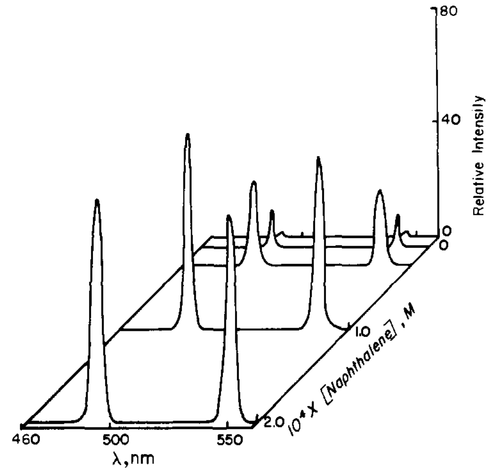

Figure 4. Three-dimensional plot for the changes of emission spectra of 0.01 M $TbCl_3$ as a function of increasing naphthalene concentration. Excited at 282 nm.

The enhanced intensity of Tb(III) luminescence was found to be dependent on both the $TbCl_3$ and naphthalene concentrations (Table II). Increasing the naphthalene concentration in the 1.0×10^{-5} to 1.0×10^{-3} M range resulted in a sigmoidal increase of the relative emission intensity of Tb(III) up to a maximum after which there is a decrease. Since the observed decrease of fluorescence intensity at higher donor concentration was found to be dependent on the geometry of the system (e.g., the decrease observed at right angle emission was not

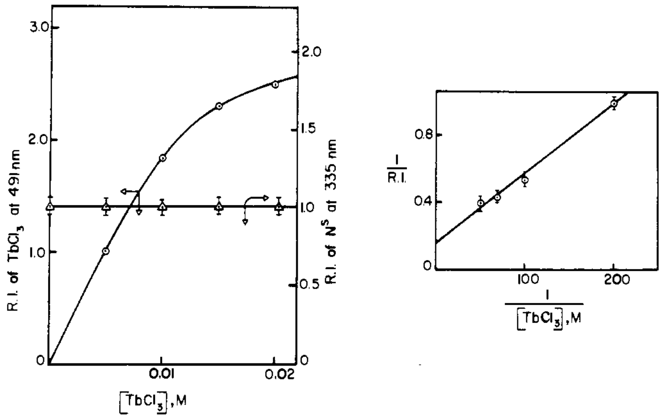

Figure 5. Plot of relative luminescence intensities of $TbCl_3$ and naphthalene in 0.20 M SDS in the presence of 0.01 M sodium acetate-acetic acid buffer at pH 5.0 against $TbCl_3$ concentration (left). Double reciprocal plot of relative $TbCl_3$ luminescence against $TbCl_3$ concentration (right).

Table III. Naphthalene Singlet Lifetime as a Function of Naphthalene and $TbCl_3$ Concentrations[a]

10^4[naphthalene], M	[$TbCl_3$], M	[$Tb(NO_3)_3$], M	τ, ns[b]
0.10	0.010		75.7
0.30	0.010		79.1
1.00			75.7
1.00	0.005		79.1
1.00	0.010		79.7
1.00	0.015		78.5
1.00	0.020		79.2
2.00	0.010		78.9
10.00	0.010		76.9
1.00		0.010	78.5
1.00		0.020	77.9

[a] [SDS] = 0.20 M in 0.01 M acetate buffer at pH 5.0. [b] Excitation wavelength 280 nm; emission wavelength 335 nm.

observable using front face illumination) it is attributed to an inner filter effect.[24,25] Furthermore, the decrease in Tb(III) emission intensity at 491 nm was paralleled by a decrease in the emission intensity of naphthalene singlet at 335 nm. At a constant naphthalene concentration increasing concentrations of $TbCl_3$ in 0.20 M SDS resulted in a saturation-type increase of the Tb(III) emission intensity. This saturation behavior was independent of the geometry of the system and was not paralleled by an increase of naphthalene emission (left-hand side of Figure 5). Apparently inner filter effect is not responsible here for the observed behavior. Fluorescence lifetime of the naphthalene singlet in 0.20 M SDS remained unaffected by the addition of $TbCl_3$ or by changes of either the donor or acceptor concentration (Table III). This is explicable if the singlet domain of the excited naphthalene is not involved in the energy transfer process. A similar conclusion has been reached for several energy transfer systems between organic and rare earth compounds in frozen alcohol glasses.[12]

Upon excitation at 282 nm, the luminescence spectra of 1.0 × 10^{-4} M naphthalene in the presence of 1.0 × 10^{-2} M $TbCl_3$ in 0.20 M SDS, taken 20 μs subsequent to the light flash, consisted of emission bands with maxima centered at 340-360, 491, 546, 583-589 (doublet), 623, 650, 670, and 680 nm. The emission band at 340-360 nm was attributed to the naphthalene triplet while the remaining bands were ascribed to $TbCl_3$ luminescence. The intensity of the emission of the naphthalene triplet, at 20 μs, was approximately 20-fold smaller than those due to $TbCl_3$ emission. By suitable adjustments of the delay, it was possible to follow the time dependence of the luminescence. The emission band due to the naphthalene triplet at 340-360 nm decayed with a lifetime of (1.14 ± 0.07) × 10^{-5} s. This lifetime, however, may represent quenching the naphthalene triplet by $TbCl_3$, which is present in high local concentrations at the micelle surface. Nevertheless, the decay of the naphthalene triplet was paralleled with a buildup of luminescence intensities due to $TbCl_3$. The lifetime for the buildup, observed at 491 or at 546 nm, (1.14 ± 0.07) × 10^{-5} s, were found to be identical, within experimental error, with the decay of the naphthalene triplet.

Table IV. Relative Intensities of Naphthalene Singlet Emission and $TbCl_3$ Emission in the Absence of SDS[a]

10^4[naphthalene], M	[$TbCl_3$], M	RI_{335nm}[b,c]	RI_{491nm}[b,d]
0.33	0.020		1.00
0.66	0.020		0.95
1.00	0.020	1.00	0.93
1.66	0.020		0.90
1.00	0.025	0.98	
1.00	0.035	0.95	
1.00	0.040	0.94	

[a] EtOH-H_2O, 4:1 (v/v). [b] Excitation wavelength 282 nm. [c] Emission wavelength 335 nm (naphthalene singlet). [d] Emission wavelength 491 nm ($TbCl_3$ luminescence).

Attempts to observe energy transfer in the absence of SDS were unsuccessful under the present experimental conditions (Table IV). In fact, a small decrease of fluorescence intensity is observed, with increasing concentrations of naphthalene or $TbCl_3$ presumably originating in inner filter effects.

Discussion

Photoexcitation of naphthalene (N) is described by eq 3-12:

$$^1N + h\nu \xrightarrow{k_3} {}^1N^* \quad (3)$$

$$^1N^* \xrightarrow{k_4} {}^1N + h\nu_N{}^F \quad (4)$$

$$^1N^* \xrightarrow{k_5} {}^1N \quad (5)$$

$$^1N^* + {}^1N \xrightarrow{k_6} \text{quenching} \quad (6)$$

$$^1N^* + O_2 \xrightarrow{k_7} \text{quenching} \quad (7)$$

$$^1N^* \xrightarrow{k_8} {}^3N^* \quad (8)$$

$$^3N^* \xrightarrow{k_9} {}^1N + h\nu_N{}^P \quad (9)$$

$$^3N^* \xrightarrow{k_{10}} {}^1N \quad (10)$$

$$^3N^* + O_2 \xrightarrow{k_{11}} \text{quenching} \quad (11)$$

$$^3N^* + {}^3N^* \xrightarrow{k_{12}} \text{quenching} \quad (12)$$

The singlet excited naphthalene (formed in eq 3) can return to the ground state by fluorescence emission (eq 4), by radiationless decay (eq 5), by concentration (eq 6), or by oxygen (eq 7) quenching. Alternatively, it can intersystem cross to form triplet naphthalene (eq 8). The naphthalene triplet, in turn, may decay by phosphorescence emission (eq 9) or by radiationless transition (eq 10). It can also be quenched by oxygen (eq 11) or be returned to ground state by triplet-triplet annihilation (eq 12).

If terbium chloride, Tb(III), is present along with naphthalene additional photophysical processes (eq 13-18) need to be considered:

$$(^7\mathrm{F})\mathrm{Tb(III)} + h\nu \xrightarrow{k_{13}} (^5\mathrm{D})\mathrm{Tb(III)} \qquad (13)$$

$$^1\mathrm{N}^* + (^7\mathrm{F})\mathrm{Tb(III)} \xrightarrow{k_{14}} {}^1\mathrm{N} + (^5\mathrm{D})\mathrm{Tb(III)} \qquad (14)$$

$$^3\mathrm{N}^* + (^7\mathrm{F})\mathrm{Tb(III)} \xrightarrow{k_{15}} {}^1\mathrm{N} + (^5\mathrm{D})\mathrm{Tb(III)} \qquad (15)$$

$$(^5\mathrm{D})\mathrm{Tb(III)} \xrightarrow{k_{16}} (^7\mathrm{F})\mathrm{Tb(III)} + h\nu_{\mathrm{Tb}}{}^{\mathrm{L}} \qquad (16)$$

$$(^5\mathrm{D})\mathrm{Tb(III)} \xrightarrow{k_{17}} (^7\mathrm{F})\mathrm{Tb(III)} \qquad (17)$$

$$(^5\mathrm{D})\mathrm{Tb(III)} + \mathrm{O}_2 \xrightarrow{k_{18}} \text{quenching} \qquad (18)$$

Terbium chloride may be excited directly (eq 13) or alternatively it can act as an energy acceptor from singlet (eq 14) or triplet (eq 15) naphthalene. The excess energy of the terbium cation may be dissipated by returning to the ground state via luminescence (eq 16), radiationless decay (eq 17), or by oxygen quenching (eq 18).

Under the present experimental conditions ([micelle] = 2 × 10^{-3} M and [naphthalene] = 10^{-5}-10^{-3} M) there is less than one molecule of naphthalene per micelle; self-quenching (eq 6) and triplet-triplet annihilation (eq 12) are, therefore, unlikely to be important. Sufficient degassing obviates the possibility of oxygen quenching (eq 7 and 11 may be neglected). Irradiation at 282 nm and at relatively low intensities ensures energy deposition predominantly in naphthalene, since the molar absorptivities of naphthalene are far in excess of that of $\mathrm{TbCl_3}$. Furthermore, the intensity of $\mathrm{TbCl_3}$ emission is approximately 100 times less than that observed in the presence of naphthalene, rendering eq 15 to be the main photophysic pathway for excitation of $\mathrm{TbCl_3}$ and thus allowing the neglect of eq 13. Additionally, energy transfer from singlet naphthalene to the terbium cation is spin forbidden (eq 14). Taking advantage of these simplications, the observed luminescence intensity of terbium(III)chloride, L_{Tb}, in the presence of micelle solubilized naphthalene can be described by

$$\mathrm{L_{Tb}} = k_{16}[(^5\mathrm{D})\mathrm{Tb(III)}] = \frac{(k_5 + k_8)k_{16}k_{15}I_{\mathrm{N}}[(^7\mathrm{F})\mathrm{Tb(III)}]}{(k_{16} + k_{17})(k_9 + k_{10} + k_{15}[(^7\mathrm{F})\mathrm{Tb(III)}])(k_4 + k_5 + k_8)} \qquad (19)$$

where I_{N} is the fluorescence intensity of naphthalene in the absence of terbium chloride, governed by eq 3. Equation 19 is analogous to that utilized in the triplet-triplet energy transfer mechanism of organic molecules[26] and it can be rearranged to

$$\frac{1}{L_{\mathrm{Tb}}} = \frac{k_{15}\tau_{\mathrm{N}}\mathrm{T}}{(k_5 + k_8)k_{16}k_{15}I_{\mathrm{N}}\tau_{(^5\mathrm{D})\mathrm{Tb(III)}}\tau_{\mathrm{N}}\mathrm{T}\tau_{\mathrm{N}}\mathrm{S}} + \frac{1}{(k_5 + k_8)k_{16}k_{11}I_{\mathrm{N}}\tau_{(^5\mathrm{D})\mathrm{Tb(III)}}\tau_{\mathrm{N}}\mathrm{T}\tau_{\mathrm{N}}\mathrm{S}[^7(\mathrm{F})\mathrm{Tb(III)}]} \qquad (20)$$

where $\tau_{(^5\mathrm{D})\mathrm{Tb(III)}}$, $\tau_{\mathrm{N}}\mathrm{T}$, and $\tau_{\mathrm{N}}\mathrm{S}$ are luminescence lifetime of terbium chloride, phosphorescence lifetime of naphthalene, and fluorescence lifetime of naphthalene, respectively, and are defined as $\tau_{(^5\mathrm{D})\mathrm{Tb(III)}} = 1/(k_{16} + k_{17})$, $\tau_{\mathrm{N}}\mathrm{T} = 1/\ (k_9 + k_{10})$, and $\tau_{\mathrm{N}}\mathrm{S} = 1/(k_4 + k_5 + k_8)$. A plot of the left-hand side of eq 20 against the reciprocal concentration of terbium chloride should result in a straight line. The ratio of the intercept to the slope of this line, $k_{15}\tau_{\mathrm{N}}\mathrm{T}$, is referred to as the triplet sensitization constant, $K_{\mathrm{S}}\mathrm{T}$.[26] Since this ratio is independent of the numerical values assigned to the luminescence we have arbitrarily chosen a value of one for the luminescence intensity due to the lowest concentration of terbium chloride (0.005 M) and have expressed luminescences at other terbium chloride concentrations relative to this value. This relative luminescence intensities, RI values, plotted linearly according to eq 20 (right-hand side of Figure 5) and gave 40 M^{-1} for the naphthalene triplet sensitization constant. The rate constant for energy transfer between naphthalene triplet and terbium chloride, k_{15}, was estimated from the Stokes-Einstein relationship

$$k_{15} = \frac{8RT}{3000\eta} \qquad (21)$$

to be 7 × 10^7 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at T = 398 K using η = 92 cP for the microscopic viscosity of the SDS micelle.[27] Substituting this value for k_{15} resulted in a lifetime of micelle solubilized naphthalene triplet of 5.7 × 10^{-7} s.

Triplet lifetime of the naphthalene donor can be alternatively obtained without an a priori assumption of detailed photophysics. Heller and Wasserman proposed that the ratio of the observed intensity of rare earth emission at any concentration to that at saturation, y, depends on the acceptor concentration according to[12]

$$y = \frac{k_{15}[\mathrm{Tb(III)}]}{k_{15}[\mathrm{Tb(III)}] + k_{\mathrm{N}}{}^{\mathrm{T}}} \qquad (22)$$

where $k_{\mathrm{N}}{}^{\mathrm{T}}$ is the first-order rate constant for the donor triplet quenching reaction and is equal to $1/\tau_{\mathrm{N}}\mathrm{T}$. A plot of $1/y$ vs. $1/[\mathrm{Tb(III)}]$ gives a good straight line (not shown). The slope of this line, $k_{\mathrm{N}}{}^{\mathrm{T}}/k_{15}$, yields 5.7 × 10^{-7} s for the lifetime of the naphthalene triplet upon substituting the value for k_{15} (vide supra). The agreement of triplet lifetimes derived by these two methods is hardly surprising since eq 22 can be derived from eq 20 in conjunction with the appropriate photophysical processes.

The use of eq 21 may be questionable since true diffusion is not involved (k_{15} = 7 × 10^7 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$). Indeed the lifetime estimated for the naphthalene triplet in micellar SDS by means of eq 21 (5.7 × 10^{-7} s) is shorter than that reported in fluid hydrocarbons at 25 °C (~10^{-5} s).[28] The directly determined lifetime, $\tau_{\mathrm{N}}\mathrm{T}$ = (1.14 ± 0.07) × 10^{-5} s (see Results), is in accord, however, with the reported value for $\tau_{\mathrm{N}}\mathrm{T}$ for naphthalene in fluid hydrocarbons at 25 °C (~10^{-5} s).[28] The agreement between $\tau_{\mathrm{N}}\mathrm{T}$ and the lifetime due to the buildup of $\mathrm{TbCl_3}$ luminescence substantiates the postulated mechanism for energy transfer.

Requirements of the observed enrgy transfer are twofold. First, the energy level of the donor has to be similar to that required for raising an acceptor molecule to its excited state.[24,26] This requirement is clearly met. The naphthalene triplet energy is in the order of 21 250-21 300 cm^{-1} in hydrocarbon solvents[24] and it is relatively independent of solvent changes.[24] The $^7\mathrm{F}_6 \rightarrow {}^5\mathrm{D}_4\mathrm{Tb(III)}$ transition with emission at 491 nm (20 370 cm^{-1})[12] appropriately matches the donor for the required optimum overlap for energy transfer. The second requirement for energy transfer is that the micelle solubilized naphthalene triplet can diffuse to the terbium chloride, bound at the Stern layer, within its lifetime. The time needed, t, for a naphthalene molecule to diffuse from the micellar interior to the Stern layer may be estimated by the use of Fick's diffusion theory

$$t = \frac{\overline{\chi}^2\, 3\pi\eta}{KT} \qquad (23)$$

where $\overline{\chi}$ is the mean path length, taken as 20 Å for the radius of an SDS mcielle,[2] η is the microscopic viscosity (92 cP),[27] K is the Boltzmann constant, and T is the absolute temperature. Substituting these values into eq 23 leads to 262 ns as the time required for a naphthalene molecule to diffuse from the interior of an SDS micelle to the surface. The significant fact is that naphthalene triplet is sufficiently long lived [$\tau_N T \geq (1.14 \pm 0.07) \times 10^{-5}$ s] to diffuse out of the micellar interior and transfer its energy to terbium chloride.

The role of micelles is the simple, albeit vital, compartmentalization of the energy transfer partners. It separates naphthalene molecules from each other obviating thereby triplet–triplet annihilation (reaction 12). Additionally, by binding the terbium chloride electrostatically to the negatively charged micellar surface, the effective concentration of the acceptor molecules is substantially increased. The concentration of countercations in the micellar Stern layer has been estimated to be 3.0 M.[29] In aqueous solution reaction 12 successfully competes with reaction 15 and thus energy transfer is not observable. These results emphasize the important roles artificial and real membranes play in enhancing the efficiency of energy transfer.

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Electrochemiluminescence from the Thianthrene–2,5-Diphenyl-1,3,4-oxadiazole System. Evidence for Light Production by the T Route

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Abstract: The chemiluminescent reaction between the thianthrene (TH) cation radical and the anion radical of 2,5-diphenyl-1,3,4-oxadiazole (PPD) has been studied by the triple step technique. Emission transients decay very quickly and their magnitudes are extremely sensitive to the surface condition of the electrode. The current during the second step adheres very closely to that predicted by digital simulation, and this agreement is taken as evidence that the diffusion patterns in solution are accurately modeled by the simulation. The light intensity is proportional to the square of the redox reaction rate. This observation is incompatible with the generation of any significant component of luminescence by the S route. It does correspond to a limiting case of pure T-route behavior. A new type of experiment, in which the electrode is pulsed back to the initial potential for a brief interval during the second step, has demonstrated unequivocally that the chemiluminescence arises after a few milliseconds from a solution phase reaction zone, rather than from the electrode surface. Absolute light measurements give an emission efficiency, ϕ_{ecl}, on the order of 10^{-4}. The precise value is highly dependent on conditions.

The electron transfer reaction between the radical cation of thianthrene (TH) and the radical anion of 2,5-diphenyl-1,3,4-oxadiazole (PPD) yields light mainly from the first excited singlet state of thianthrene, $^1TH^*$.[1] Keszthelyi, Tachikawa, and Bard showed early that this system follows the pattern of behavior that is generally associated with the so-called S route to chemiluminescence,[1-3] in which the emitting singlet is populated directly in the redox event itself.

$$TH^+ + PPD^- \rightarrow {}^1TH^* + PPD \qquad (1)$$

$$^1TH^* \rightarrow TH + h\nu \qquad (2)$$

That is, the redox process is energetic enough to populate $^1TH^*$ (see Table I), and there is no magnetic effect on the chemiluminescence.

Magnetic effects have been used frequently as a diagnostic tool for the differentiation of mechanisms for redox chemiluminescence.[1-7] Enhancements of emission with increasing field strength have been observed for every studied case of energy-deficient luminescence (i.e., one involving a redox reaction that